Generalized Multicomponent Equation for Activity Coefficient Calculation

A new model for the prediction of liquid phase activity coefficients used for predicting multicomponent phase equilibria is presented and compared with presently available methods for making these calculations. In its binary form, the new model includes Margules, van Laar, NRTL, Scatchard-Hamer, and Fariss models as special cases. In its multicomponent form the van Laar, Margules, and Scatchard-Hamer forms are different from and superior to the Wohl expansion. It is also possible with the new model to use different special case models for each of the binary pairs.

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SCOPE

In the design of processes for vapor-liquid, liquid-liquid, or solid-liquid separations the calculation of liquid phase activity coefficients is of critical significance. There has been a proliferation of equations proposed for calculating the activity coefficient, and a surprisingly large number have survived primarily because no single equation has been proposed which can represent all types of solutions.

Wohl (1946), in a classical paper in 1946 showed how the useful equations of that time (Margules, 1895; Scatchard-Hamer, 1952; van Laar, 1910) could be represented as special cases within a single framework of generalized equations, and how the binary forms could be extended to multicomponent systems. There were relatively few new equations presented after Wohl's work until 1964. Since that time there has been a flurry of equations which could not be taken as special cases of the Wohl generalized equations. The most significant of these are the Wilson equations (Wilson, 1964) and the NRTL equations of Renon and Prausnitz (1968).

In spite of the availability of all these separate equations, it is still necessary occasionally to develop special equations for some systems. For example, sometimes a particular binary pair of a multicomponent system will exhibit an interior maximum activity coefficient. The Margules equations are particularly well suited to such a binary but are often unsatisfactory for the remaining binary pairs.

It would be valuable, however, to develop a set of thermodynamically consistent equations in which two or more different binary equations could be mixed in the multicomponent computations. The results of the effort to do so are presented in this paper. A generalized set of equations has been developed which includes, as special cases, the binary form of any of the Wohl three suffix equations (Margules, Scatchard-Hamer, van Laar), Fariss Equations (Null, 1970) and the NRTL equations of Renon and Prausnitz. The multicomponent form of the van Laar, Margules, and Scatchard-Hamer equations differs from the Wohl expansion and requires binary parameters only. It has been shown by Renon and Prausnitz that the NRTL equations, by the adjustment of an extra parameter, can be made to virtually reproduce the Wilson binary equations. The Fariss equations also have the ability to virtually reproduce the Wilson equation with the appropriate choice of the third parameter while reducing identically to the van Laar equations when the third constant is zero. Further, the new equations provide a means of expanding Fariss' equations to multicomponent systems. Thus, this work incorporates into a single set of equations the ability to duplicate all the more commonly used equations now available for calculating activity coefficients. Furthermore, it also provides the capability of mixing the forms.

CONCLUSIONS AND SIGNIFICANCE

A generalized multicomponent equation for activity coefficients has been developed as

$$\ln \gamma_k = \frac{1}{2}\left\{\frac{\left(\sum_j A_{jk}x_j\right)\left(\sum_j R_{jk}x_j\right)}{\left(\sum_j V_{jk}x_j\right)\left(\sum_j S_{jk}x_j\right)} + \sum_i x_i \frac{\left(\sum_j A_{ji}x_j\right)\left(\sum_j R_{ji}x_j\right)}{\left(\sum_j S_{ji}x_j\right)\left(\sum_j V_{ji}x_j\right)} \cdot \left[\frac{A_{ki}}{\sum_j A_{ji}x_j} + \frac{R_{ki}}{\sum_j R_{ji}x_j} - \frac{S_{ki}}{\sum_j S_{ji}x_j} - \frac{V_{ki}}{\sum_j V_{ji}x_j}\right]\right\}$$

In its binary form this equation can be made identical to any of several forms of well-known equations by making the following assumptions:
For all the special cases:

$$R_{ji} = \frac{A_{ji}}{A_{ij}}; \quad A_{ii} = 0; \quad \frac{A_{ii}}{A_{ii}} = 1$$

Van Laar:

$$V_{ji} = S_{ji} = A_{ji}/A_{ij}$$

Monsanto Modified van Laar:

$$V_{ji} = S_{ji} = |A_{ji}/A_{ij}|$$

Margules:

$$V_{ji} = S_{ji} = 1$$

Scatchard-Hamer:

$$V_{ji} = S_{ji} = v_j/v_i$$

NRTL:

$$S_{ji} = R_{ji} = \frac{A_{ji}}{A_{ij}}; \quad A_{ji} = 2\tau_{ji}G_{ji}; \quad V_{ji} = G_{ji}$$

where $G_{ji} = \exp(-\alpha_{ji}\tau_{ji})$ and $\alpha_{ji} = \alpha_{ij}$

Fariss:

$$V_{ij} = V_{ji} = \tfrac{1}{2}[\beta_{ij} + 2 + \sqrt{(\beta_{ij}+2)^2 - 4}]$$

$$A_{ij} = \frac{2V_{ij}(\ln \gamma_{ij}^{\infty})}{V_{ij} \pm 1}$$

Use + for positive deviations
Use + for negative deviations
Use − for mixed deviations

$A_{ii} = 0; \quad R_{ii} = 1; \quad S_{ii} = 1; \quad V_{ii} = 1$
$R_{ij} = 1$

$$S_{ij} = \left| \frac{A_{ij}}{A_{ji}} \right|$$

where $\beta_{ij} = \beta_{ji} \geq 0$

In the multicomponent expansion, the van Laar, Margules, and Scatchard-Hamer expansions are different from those presented by Wohl. The most significant difference is that only binary parameters are needed, whereas the Wohl expansion contains parameters that can only be evaluated from multicomponent data. It is also worth noting that the new equations require no particular relationship between the binary pair parameters of the van Laar form to prevent ambiguity in the multicomponent form, whereas the Wohl equations do. Furthermore, it is possible with the new equations to mix types. For example, in a ternary system the Margules assumptions could be applied to one binary pair, the van Laar to the second pair, and the NRTL to a third. Such mixing is not possible in any equations previously presented in the literature.

In order to test the value of the current method of expansion, the vapor-liquid equilibrium data for 10 ternary systems were compared with predictions from binary data (see Table 1). The methods of prediction compared were the Wohl expansion of the four suffix Margules equation (3 binary parameters and one ternary parameter required), the Wilson Equations (two binary parameters required), the NRTL Equations (three binary parameters), and the current expansion using the Monsanto modified van Laar assumptions for all binaries (two binary parameters). In every case in which no alcohol-hydrocarbon binary was involved, the current van Laar expansion gave the lowest standard deviation in calculated vapor mole fractions and total pressure. When an alcohol-hydrocarbon pair was involved, the NRTL equation generally gave better results. This result is not surprising since the van Laar equation is known to give poor results for alcohol-hydrocarbon binary systems. No systematic attempt has been made to mix the Margules, NRTL, and van Laar binary assumptions since the number of combinations to be tested would be much too large. However, one would presume that the use of the binary assumptions that gives the best representation of each binary pair would be likely to give the best ternary prediction. This presumption has been verified in several simulations involving proprietary processes. When the Wilson equations give the best two parameter representation of a binary, the NRTL equation can be used by choosing the α, τ_{12}, τ_{21} combination which most nearly duplicates the Wilson equation. Renon and Prausnitz (1968) have shown that this can generally be done.

DERIVATION OF THE GENERAL EQUATION

The excess Gibbs free energy of mixing for all the forms to be derived can be expressed as

$$Q = \frac{g^E}{RT} = \frac{1}{2}\sum_i x_i \frac{\left(\sum_j A_{ji}x_j\right)\left(\sum_j R_{ji}x_j\right)}{\left(\sum_j V_{ji}x_j\right)\left(\sum_j S_{ji}x_j\right)} \quad (1)$$

When the excess free energy is expressed in this form, the activity coefficient is given by

$$\ln \gamma_k = Q + \frac{\partial Q}{\partial x_k} - \sum_j x_j \frac{\partial Q}{\partial x_j}$$

For equations of the form of Equation (1),

$$\frac{\partial Q}{\partial x_k} = \frac{1}{2}\left\{ \frac{\left(\sum_j A_{jk}x_j\right)\left(\sum_j R_{jk}x_j\right)}{\left(\sum_j V_{jk}x_j\right)\left(\sum_j S_{jk}x_j\right)} + \sum_i x_i \frac{\left(\sum_j A_{ji}x_j\right)\left(\sum_j R_{ji}x_j\right)}{\left(\sum_j S_{ji}x_j\right)\left(\sum_j V_{ji}x_j\right)} \cdot \left[\frac{A_{ki}}{\sum_j A_{ji}x_j} + \frac{R_{ki}}{\sum_j R_{ji}x_j} - \frac{S_{ki}}{\sum_j S_{ji}x_j} - \frac{V_{ki}}{\sum_j V_{ji}x_j} \right] \right\} \quad (2)$$

$\sum_m x_m \frac{\partial Q}{\partial x_m}$, for expansions of the form of Equation (1) can be evaluated as follows

$$\sum_m x_m \frac{\partial Q}{\partial x_m} = \frac{1}{2}\left\{ \sum_m x_m \frac{\left(\sum_j A_{jm}x_j\right)\left(\sum_j R_{jm}x_j\right)}{\left(\sum_j V_{jm}x_j\right)\left(\sum_j S_{jm}x_j\right)} + \sum_i x_i \frac{\left(\sum_j A_{ji}x_j\right)\left(\sum_j R_{ji}x_j\right)}{\left(\sum_j S_{ji}x_j\right)\left(\sum_j V_{ji}x_j\right)} \cdot \left[\frac{\sum_m A_{mi}x_m}{\sum_j A_{ji}x_j} + \frac{\sum_m R_{mi}x_m}{\sum_j R_{ji}x_j} - \frac{\sum_m S_{mi}x_m}{\sum_j S_{ji}x_j} - \frac{\sum_m V_{mi}x_m}{\sum_j S_{ji}x_j} \right] \right\}$$

$$= \frac{1}{2}\left\{ 2Q + \sum_i x_i \frac{\left(\sum_j A_{ji}x_j\right)\left(\sum_j R_{ji}x_j\right)}{\left(\sum_j S_{ji}x_j\right)\left(\sum_j S_{ji}x_j\right)} \right.$$

$$\cdot (1 + 1 - 1 - 1) \Big\} = Q$$

Thus,

$$\ln \gamma_k = \frac{\partial Q}{\partial x_k} \tag{3}$$

Equation (3) is not a general equation for all forms of Q equation; it only applies when Q is given by the form of Equation (1).

The more familiar equations can be derived by various assumptions regarding the A, R, S, and V arrays. Equation (2) can be written for a binary system in which $V_{ij} = S_{ij}$, $R_{ij} = A_{ij}/A_{ji}$, $A_{ii} = 0$, and $A_{ii}/A_{ii} = 1$ as follows:

$$2 \ln \gamma_1 = \frac{A_{21}x_2\left(x_1 + \frac{A_{21}}{A_{12}}x_2\right)}{(S_{11}x_1 + S_{21}x_2)^2} + \frac{A_{21}x_1x_2}{(S_{11}x_1 + S_{21}x_2)^2} - \frac{2S_{11}A_{21}x_1x_2\left(x_1 + \frac{A_{21}}{A_{12}}x_2\right)}{(S_{11}x_1 + S_{21}x_2)^3} + \frac{A_{12}x_2\left(\frac{A_{12}}{A_{21}}x_1 + x_2\right)}{(S_{12}x_1 + S_{22}x_2)^2} + \frac{\frac{A^2_{12}}{A_{21}}x_1x_2}{(S_{12}x_1 + S_{22}x_2)^2} - \frac{2S_{12}A_{12}x_1x_2\left(\frac{A_{12}}{A_{21}}x_1 + x_2\right)}{(S_{12}x_1 + S_{22}x_2)^3} \tag{4}$$

If we further let $S_{11} = S_{22} = 1$ and $S_{12} = 1/S_{21}$, Equation (4) becomes

$$2 \ln \gamma_1 = \frac{A_{21}x_2\left(x_1 + \frac{A_{21}}{A_{12}}x_2\right)}{(x_1 + S_{21}x_2)^2} + \frac{A_{21}x_1x_2}{(x_1 + S_{21}x_2)^2} - \frac{2A_{21}x_1x_2\left(x_1 + \frac{A_{21}}{A_{12}}x_2\right)}{(x_1 + S_{21}x_2)^3} + \frac{S^2_{21}A_{12}x_2\left(\frac{A_{12}}{A_{21}}x_1 + x_2\right)}{(x_1 + S_{21}x_2)^2} + \frac{S^2_{21}\frac{A^2_{12}}{A_{21}}x_1x_2}{(x_1 + S_{21}x_2)^2} - \frac{2S^2_{21}A_{12}x_1x_2\left(\frac{A_{12}}{A_{21}}x_1 + x_2\right)}{(x_1 + S_{21}x_2)^3} \tag{5}$$

If we now define

$$Z_1 \equiv \frac{x_1}{x_1 + S_{21}x_2}; \quad Z_2 \equiv \frac{S_{21}x_2}{x_1 + S_{21}x_2} \tag{6}$$

we can substitute Equations (6) into (5) and collect like terms to obtain

$$\ln \gamma_1 = Z_2^2\left[\frac{S^2_{12}A^2_{21} + A^2_{12}}{2A_{12}}\right] + 2Z_1Z_2^2\left\{\frac{A^2_{21} + S^2_{21}A^2_{12}}{2S_{21}A_{21}} - \frac{S^2_{12}A^2_{21} + A^2_{12}}{2A_{12}}\right\} \tag{7}$$

Equation (7) is identical to the general Wohl three suffix binary expansion if we recognize that

$$S_{21} \sim \frac{q_2}{q_1}$$

$$A'_{12} = \ln \gamma_1^{\infty} \sim \frac{S^2_{12}A^2_{21} + A^2_{12}}{2A_{12}} \tag{8}$$

$$A'_{21} = \ln \gamma_2^{\infty} \sim \frac{S^2_{21}A^2_{12} + A^2_{21}}{2A_{21}}$$

of the Wohl expansion. When Equation (8) is substituted into Equation (7) we get the binary three-suffix Wohl equation:

$$\ln \gamma_1 = Z_2^2\left[A'_{12} + 2Z_1\left(\frac{q_2}{q_1}A'_{21} - A'_{12}\right)\right] \tag{9}$$

From Equation (9) we may, of course, make the usual assumptions to obtain van Laar, Margules, and Scatchard-Hamer equations and obtain the relationship between $\ln \gamma^{\infty}$ and the parameters of the equations:

Margules: $\frac{q_1}{q_2} = 1$; $Z = x$

$$\ln \gamma_1 = x_2^2\left[A'_{12} + 2x_1\left(A'_{21} - A'_{12}\right)\right] \tag{10}$$

$$A_{12} = \frac{2 \ln \gamma_1^{\infty}}{1 + \left(\frac{\ln \gamma_1^{\infty}}{\ln \gamma_2^{\infty}}\right)^2}, \quad A_{21} = \frac{2 \ln \gamma_2^{\infty}}{1 + \left(\frac{\ln \gamma_2^{\infty}}{\ln \gamma_1^{\infty}}\right)^2} \tag{11}$$

Scatchard-Hamer: $\frac{q_1}{q_2} = \frac{v_1}{v_2}$; $Z = \phi =$ volume fraction

$$\ln \gamma_1 = \phi_2^2\left[A'_{12} + 2\phi_1\left(\frac{v_1}{v_2}A'_{21} - A'_{12}\right)\right] \tag{12}$$

$$A_{12} = \frac{2 \ln \gamma_1^{\infty}}{1 + \left(\frac{v_2 \ln \gamma_1^{\infty}}{v_1 \ln \gamma_2^{\infty}}\right)^2}, \tag{13}$$

$$A_{21} = \frac{2 \ln \gamma_2^{\infty}}{1 + \left(\frac{v_1 \ln \gamma_2^{\infty}}{v_2 \ln \gamma_1^{\infty}}\right)^2}$$

Van Laar: $\frac{q_1}{q_2} = \frac{A_{12}}{A_{21}}$

$$\ln \gamma_1 = A_{12}Z_2^2 \tag{14}$$

$$A_{12} = \ln \gamma_1^{\infty}, \quad A_{21} = \ln \gamma_2^{\infty} \tag{15}$$

Monsanto Modified van Laar: $\frac{q_1}{q_2} = \left|\frac{A_{12}}{A_{21}}\right|$

$$\ln \gamma_1 = A_{12}Z_2^2\left[1 + 2Z_1\left(\frac{A_{12}A_{21}}{|A_{12}A_{21}|} - 1\right)\right] \tag{16}$$

$$A_{12} = \ln \gamma_1^{\infty}, \quad A_{21} = \ln \gamma_2^{\infty} \tag{17}$$

Particular note should be made of the fact that, while the new equations can be reduced to the indicated binary form of the Wohl equations, the multicomponent expansions are entirely different from the multicomponent Wohl expansions. In particular, the equations developed here require no specific ternary information, and there is no ambiguity in the multicomponent van Laar form. This and other features are discussed further in the next section.

The NRTL equations of Renon and Prausnitz can also be represented as a special case of the new equations. If we assume

$$S_{ji} = R_{ji} = \frac{A_{ji}}{A_{ij}},$$

$$V_{ji} = G_{ji}$$

$$A_{ji} = 2\tau_{ji}G_{ji}$$

where $G_{ji} = \exp(-\alpha_{ji}\tau_{ji})$ and $\alpha_{ij} = \alpha_{ji}$

we get

$$Q = \sum_i x_i \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_j G_{ji} x_j} \tag{18}$$

which is identical to the Q equation presented by Renon and Prausnitz. The relationship between the parameters and infinite dilution activity coefficients of binary systems is given by

$$\ln \gamma_1^\infty = \tau_{21} + \tau_{12} \exp(-\alpha_{12}\tau_{12})$$
$$\ln \gamma_2^\infty = \tau_{12} + \tau_{21} \exp(-\alpha_{12}\tau_{21}) \tag{19}$$

For a given α, the τ's can be numerically evaluated from Equations (19). The equations developed by Fariss can be obtained if we assume

$$R_{ii} = R_{ij} = S_{ii} = V_{ii} = 1$$
$$A_{ii} = 0$$
$$V_{ij} = V_{ji}$$
$$S_{ij} = \left| \frac{A_{ij}}{A_{ji}} \right|$$

from which

$$Q = \frac{1}{2} \sum_i x_i \frac{\sum_j A_{ji} x_j}{\left(\sum_j V_{ji} x_j\right)\left(\sum_j S_{ji} x_j\right)} \tag{20}$$

For the binary case, we get after algebraic manipulation

$$Q = \frac{A_{12}A_{21}x_1x_2\left[\frac{|A_{12}|}{A_{12}}x_2 + \frac{|A_{21}|}{A_{21}}x_1 + V\left(\frac{|A_{12}|}{A_{12}}x_1 + \frac{|A_{21}|}{A_{21}}x_2\right)\right]}{2V(|A_{12}|x_1 + |A_{21}|x_2)\left(1 + \frac{[V-1]^2}{V}x_1x_2\right)} \tag{21}$$

A_{12} and A_{21} are related to γ^∞ as follows:

$$A_{12} = \frac{2V}{V \pm 1} \ln \gamma_1^\infty \tag{22}$$

where the negative sign is used only for mixed deviations where $V \neq 1$. When both deviations are of the same sign (the only case considered by Fariss) Equation (21) reduces to

$$Q = \frac{A_{12}A_{21}x_1x_2(V+1)}{2V(A_{12}x_1 + A_{21}x_2)\left(1 + \frac{(V-1)^2}{V}x_1x_2\right)} \tag{23}$$

The Fariss form is

$$Q = \frac{A'_{12}A'_{21}x_1x_2}{(A'_{12}x_1 + A'_{21}x_2)(1 + \beta x_1x_2)} \tag{24}$$

Equations (23) and (24) are identical if we note the correspondence:

$$A_{ij} = \frac{2V}{V+1}A'_{ij} \quad \text{and} \quad \beta = \frac{(V-1)^2}{V}.$$

As a final comment, it should be noted that the same assumptions do not need to be made for all the binary pairs of a multicomponent mixture. Thus, the facility is available for mixing assumptions. This facility can be especially important when the various binary pairs are fit best by different binary equations.

TERNARY FORM

The ternary form of Equation (2) after applying the van Laar assumptions and simplification for component 1 is

$$\ln \gamma_1 = \frac{1}{2}\left[\frac{\left(\frac{A_{21}}{A_{12}}\right)^2 x_2^2 A_{12} + x_2x_3\left(\frac{A_{31}}{A_{13}}A_{21} + \frac{A_{21}}{A_{12}}A_{31}\right) + \left(\frac{A_{31}}{A_{13}}\right)^2 x_3^2 A_{13}}{\left(x_1 + \frac{A_{21}}{A_{12}}x_2 + \frac{A_{31}}{A_{13}}x_3\right)^2}\right.$$
$$+ \frac{A_{12}x_2^2 + x_2x_3\left(\frac{A_{32}}{A_{23}}A_{12} - \frac{A_{12}}{A_{21}}A_{32}\right)}{\left(\frac{A_{12}}{A_{21}}x_1 + x_2 + \frac{A_{32}}{A_{23}}x_3\right)^2}$$
$$\left. + \frac{A_{13}x_3^2 + x_2x_3\left(\frac{A_{23}}{A_{32}}A_{13} - \frac{A_{13}}{A_{31}}A_{23}\right)}{\left(\frac{A_{13}}{A_{31}}x_1 + \frac{A_{23}}{A_{32}}x_2 + x_3\right)^2}\right] \tag{25}$$

as compared to Wohl's ternary van Laar equation,

$$\ln \gamma_1 = \frac{\left(\frac{A_{21}}{A_{12}}\right)^2 x_2^2 A_{12} + x_2x_3\left(\frac{A_{31}}{A_{13}}A_{21} + \frac{A_{21}}{A_{12}}A_{31} - \frac{A_{12}}{A_{21}}A_{32}\right) + \left(\frac{A_{31}}{A_{13}}\right)^2 x_3^2 A_{13}}{\left(x_1 + \frac{A_{21}}{A_{12}}x_2 + \frac{A_{31}}{A_{13}}x_3\right)^2} \tag{26}$$

Equation (25) is symmetrical in that the subscript 2 and 3 can be interchanged with no effect on the activity coefficient of component 1. Equation (26) does not have such a property. However, Equations (25) and (26) become identical to each other and to the ternary three-suffix Margules form for systems of uniform parameters; that is,

$$A_{12} = A_{21} = A_{31} = A_{13} = A_{23} = A_{32} = A;$$

they all become

$$\ln \gamma_1 = A[x_2^2 + x_2x_3 + x_3^2].$$

For systems of binary symmetry, that is,

$$A_{ij} = A_{ji}$$

Equation (25) and the ternary Wohl's expansion of the Margules equation give the same results.

TERNARY ISOGAMMA PLOTS

In order to show the behavior of various representations of activity coefficient without referring to their individual assumed forms of molecular interaction, a plot of constant ln γ_1 has been prepared in Figure 1 for a uniform ternary system. For this plot ln γ_{ij}^{∞} is the infinite dilution activity coefficient of component i in solution of j. For comparison in the same plot are shown results using the three NRTL equations and the general equation with van Laar assumptions for all binary pairs. All four sets of curves are symmetrical with respect to the center line.

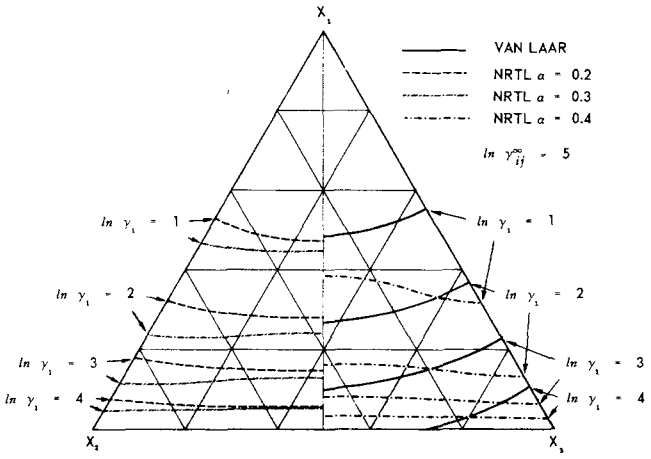

Fig. 1. Constant ln γ_1 plot of a uniform ternary system (All ln γ_{ij}^{∞}'s identically 5).

The ln γ_1 predicted by the new van Laar equation (and also the Margules three suffix equation) decreases slowly as x_1 increases. It also shows a depression in the center more pronounced than the Wilson equation.

The behavior of ln γ_1 predicted by the NRTL equations is most interesting. The rate of the ln γ_1 decrease as x_1 increases is very sensitive to α which is the third parameter appearing in a negative exponential of the equation. It exhibits characteristics of a high order equation in that it drops first as it moves away from the bound but rises as it approaches the center. The magnitude of α controls the amount of rise and fall. Figure 2 shows the value of ln γ_1^{∞} of the same system on the composition line $x_1 = 0$. The new multicomponent van Laar equation shows the largest drop in value of ln γ_1 as compared to the other equations. The NRTL equation displays a special characteristic of rising ln γ_1 in the middle of the composition range. The rise in the middle is higher for larger α although in a

TABLE 1. COMPARISON OF RESULTS USING 10 SYSTEMS

System	Temp. or pressure	No. of data points	Mean arithmatic deviation in y for individual component × 1000 (1) Wilson	(1) NRTL	(2) Wohl	(3) Van Laar	95% Confidence limit on y × 1000 (1) NRTL	(2) Wohl	(3) Van Laar	Mean arithmatic relative deviation in pressure × 1000 (1) Wilson	(1) NRTL	(3) Van Laar	95% Confidence limit on pressure × 1000 (1) NRTL	(3) Van Laar	Ref.
Methylethyl ketone	760	39	−5	−5	1	0	2	8	3	14	11	−1	33	3	*15*
Heptane	mm Hg		3	3	3	1	2	8	2						
Toluene			2	2	−4	−1	1	5	1						
Benzene	760	47	2	2	8	11	4	7	6	14	13	−20	5	11	*18*
Ethanol	mm Hg		−6	−6	−8	−13	6	8	8						
Heptane			4	4	0	2	3	4	4						
Benzene	400	50	4	3	−5	15	4	7	5	4	4	−43	9	9	*7*
Ethanol	mm Hg		−8	−7	5	−17	9	8	10						
Heptane			4	5	0	2	7	4	8						
Heptane	760	8	−2	−5	8	−5	4	16	7	−1	−7	5	9	16	*2*
Methanol	mm Hg		4	8	−6	9	8	19	11						
Toluene			−2	−3	−2	−4	5	8	6						
Methanol	35°C	6	3	4	10	−1	7	39	19	4	3	9	9	23	*12*
Carbon tetrachloride			−3	−3	3	0	4	22	8						
Benzene			0	−1	−13	1	5	20	13						
Methanol	55°C	8	3	5	8	4	7	29	13	0	2	−13	6	20	*12*
Carbon tetrachloride			−2	−2	7	−5	4	13	7						
Benzene			−1	−3	−15	1	3	21	8						
Acetone	50°C	31	−5	−5	−11	1	4	18	6	21	23	−8	16	9	*14*
Methanol			8	8	0	1	3	12	4						
Chloroform			−3	−3	11	−1	4	8	4						
Acetone	50°C	35	−4	−4	−9	−5	3	12	4	13	12	−3	12	3	*14*
Methanol			1	1	1	1	7	8	6						
Methyl acetate			3	3	8	5	5	15	5						
Ethanol	760	96	10	−4	−59	−13	7	22	3	−9	9	−7	8	4	*5*
Ethyl acetate	mm Hg		−7	5	6	23	22	57	6						
Water			−3	−1	47	−10	17	49	5						
Benzene	70°C	21	−1	−1		−3	5		4	−8	−7	0	2	1	*16*
Hexane			−2	−2		0	4		3						
Cyclohexane			3	3		2	4		3						

(1) Taken from Renon and Prausnitz (*14*).
(2) Taken from Adler, Friend and Pigford (*1*).
(3) Van Laar option of the generalized equation.

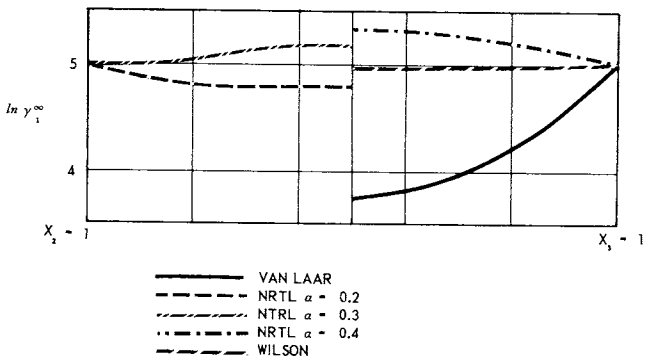

Fig. 2. In γ_1^∞ of a uniform ternary system on $x_1 = 0$.

binary system larger α causes more rapid drop in $\ln \gamma_1$ for increasing x_1.

APPLICATION TO TERNARY VLE USING ONLY BINARY PARAMETERS

One of the important roles for a general multicomponent equation is to interpolate or extrapolate the available experimental data for equilibrium calculations in process design. It is quite well known that for many binary systems, the van Laar equation gives an excellent approximation of the activity coefficients as a function of composition and can predict limited solubility. One exception is alcohol-hydrocarbon systems which are better approximated by the Wilson equation. For these systems the van Laar equations predict limited solubility when it does not exist. Since the Wilson equation cannot be used for liquid-liquid equilibrium, a three parameter NRTL equation was developed by Renon and Prausnitz. The new multicomponent van Laar equation suffers the same inadequacy as its degenerated binary form, but it is still far better than the popular multicomponent Margules form. It is not as good as the NRTL or the Wilson equations for ternary alcohol-hydrocarbon systems but slightly better for others. Table 1 summarizes the comparison of results using 10 systems. Of those systems, eight systems involve alcohol. The binary parameters were obtained by regressing the binary data using sum of squared errors in the logarithm of K, the composition ratio. The deviation in vapor mole fraction and pressure and the 95% confidence are the same as suggested by Adler et al. (1966) in their test of the multicomponent Margules equation. In their work a four-suffix Margules equation is needed to improve the fit. We have restricted the equation to the use of two parameters per pair of components in the test of the new van Laar equations. The basic equations are listed as follows:

$$\Delta y = y_c - y_e$$

$$y_{ci} = \frac{K_i x_i}{\sum_j K_j x_j}$$

$$\Delta\pi = (\pi_c - \pi_e)/\pi_e$$

$$\pi_c = \left(\sum_j K_j x_j\right) \pi_e$$

$$K_i = \frac{p_i^\bullet \gamma_i}{\pi_e}$$

where the subscript e or c denotes experimental or calculated value. π is for total pressure and $p_i^\bullet$ is the vapor pressure of component i.

Note that the vapor phase nonideality has been neglected and that normalized vapor compositions have been used in the calculation.

Table 2 shows the Antoine constants used in our study and Table 3 gives the van Laar constants. Some of the van Laar constants were not obtained through regression of data as mentioned previously. They were either available in the literature in the form of van Laar parameters or as infinite dilution activity coefficients. The sources of the data or the parameters are also given in Table 3.

Except for the systems benzene-ethanol-heptane and methanol-carbon tetrachloride-benzene the new multicomponent van Laar equation is as good as or better than either the NRTL or the Wohl's equation.

The Fariss equations were not tested in this work. However, when $\beta = 0$ Fariss equations are identical in binary and multicomponent expansions to the van Laar form. Thus, they can do no worse than the van Laar equations. Since by adjusting β they can be made to simulate the binary Wilson equations very closely, we would expect Fariss' equations to work quite well in alcohol-hydrocarbon systems also.

TABLE 2. ANTOINE CONSTANTS

Antoine constants	A	B	C
Heptane (1)	6.90240	1268.115	216.900
Benzene (1)	6.90565	1211.033	220.790
Toluene (1)	6.95464	1344.800	219.482
Ethanol (1)	8.21337	1652.050	231.480
Methyl ethyl ketone (1)	6.38469	916.010	181.840
Methanol (1)	8.07246	1574.990	238.860
Ethyl acetate (2)	7.09808	1238.71	217.000
Water (1)	7.98456	1678.95	228.970
Carbon tetrachloride (2)	6.93390	1242.43	230.000
Hexane (1)	6.87776	1171.53	224.366
Cyclohexane (1)	6.84498	1203.526	222.863

(1) API project 44, A&M College of Texas (1964).
(2) Lange, *Handbook of Chemistry*, McGraw-Hill (1967).

$$\text{Log}_{10}\, p^\bullet \text{ (mm Hg)} = A - \frac{B}{t^\circ\text{C} + C}$$

CONCLUSIONS

The equations developed in this paper provide a more accurate method of predicting multicomponent phase equilibria from binary parameters than has been available previously. Since they contain as special cases all the more commonly used activity coefficient equations previously available and provide a means of mixing them for the different binaries, their use should virtually eliminate the necessity for developing special activity coefficient equations for any system.

NOTATION

A = parameter for general activity coefficient equation
G = parameter for NRTL equation
K = phase concentration ratio, y/x
$p^\bullet$ = vapor pressure
Q = excess free energy of mixing
R = parameter for general activity coefficient equation
S = parameter for general activity coefficient equation
V = parameter for general activity coefficient equation
x = mole fraction in liquid phase
y = mole fraction in vapor phase
Z = weighted mole fraction

Greek Letters

α = parameter for NRTL equation
β = parameter for Fariss equation
γ = activity coefficient

TABLE 3. BINARY VAN LAAR CONSTANTS

System	Press. temp.	Data source	Param. source	$A_{12}T$	$A_{21}T$
Heptane-methylethyl ketone	760 mmHg	15		180.766	192.839
Toluene-methylethyl ketone	760 mmHg	15		69.716	56.143
Toluene-heptane	760 mmHg	15		41.181	54.641
Ethanol-benzene	760 mmHg	4		262.974	230.233
Heptane-benzene	760 mmHg		1	(0.232) (T)	(0.113) (T)
Heptane-ethanol	760 mmHg	3		333.311	334.045
Ethanol-benzene	45°C	3		315.250	195.489
Heptane-benzene	60°C	3		87.940	42.750
Heptane-ethanol	50°C	3		259.015	359.382
Methanol-heptane	760 mmHg	2		327.855	404.663
Toluene-heptane	760 mmHg	15		41.181	54.641
Toluene-methanol	760 mmHg	2		299.314	289.684
Carbon tetrachloride-methanol	35°C		11	206.330	439.32
Benzene-methanol	35°C		11	212.89	348.400
Benzene-carbon tetrachloride	35°C		11	32.35	16.61
Carbon tetrachloride-methanol	55°C		11	219.01	415.72
Benzene-methanol	55°C		11	224.69	340.97
Benzene-carbon tetrachloride	55°C		11	26.23	18.80
Methanol-acetone	50°C		14	(0.225) (T)	(0.305) (T)
Chloroform-acetone	50°C		14	(−0.3) (T)	(−0.36) (T)
Chloroform-methanol	50°C		14	(0.31) (T)	(0.78) (T)
Methanol-acetone	50°C		14	(0.225) (T)	(0.305) (T)
Methyl acetate-acetone	50°C		14	(0.05) (T)	(0.065) (T)
Methyl acetate-methanol	50°C		14	(0.465) (T)	(0.445) (T)
Ethyl acetate-ethanol	760 mmHg		11	109.720	120.210
Water-ethanol	760 mmHg		11	129 390	269.280
Water-ethyl acetate	760 mmHg		5	(0.8014) (T)	(1.8833) (T)
Hexane-benzene	70°C		11	62.073	59.013
Cyclohexane-benzene	70°C		11	62.948	44.151
Cyclohexane-hexane	70°C		11	3.934	6.120

°T in °K.

π = total pressure
τ = parameter for NRTL equation

Subscripts and Superscripts

i, j, k = component index
c = calculated value
e = experimental value
∞ = infinite dilution property

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